

## III.A.2 Oxidation Resistant, Cr Retaining, Electrically Conductive Coatings on Metallic Alloys for SOFC Interconnects

### Objectives

- Enable the use of inexpensive metallic alloys as planar SOFC interconnects (ICs) via protective coatings.
- Develop and demonstrate novel, cost-effective deposition processes to establish dense and uniform protective and functional coatings on metallic substrates.
- Evaluate protective coatings during exposures relevant to SOFC ICs.
- Optimize deposition process parameters to maximize SOFC metallic IC performance and ultimately reduce cost.

### Accomplishments

- Developed and tested new, hybrid surface engineering technologies combining large area filtered arc deposition (LAFAD), electron beam physical vapor deposition (EBPVD), unbalanced magnetron (UBM) and thermal evaporation to deposit dense and defect-free protective coatings in an economically favorable manner.
- Reduced metallic alloy oxidation rate by an order of magnitude. Rutherford backscattering spectroscopy (RBS) results indicate stainless steel samples with nanolayered CrN/AlN coatings exhibit an order of magnitude increase in oxidation resistance compared to uncoated counterparts. Further improvement of diffusion/oxidation barrier properties is achieved by newly developed nanolayered and/or nanocomposite MCrAlYO oxicermet coating where M=Co, Ti, Mn, or Ni.
- Developed two-segment coating architecture with bottom oxidation barrier MeCrAlO nanocomposite oxicermet segment, deposited by the LAFAD process, followed by a (Mn,Co)<sub>3</sub>O<sub>4</sub> spinel, Cr

retaining, cathode compatible segment, deposited by the hybrid filtered arc deposition (FAD)-EBPVD process.

- Significantly reduced Cr volatility. Coated samples of commercially-available 430 stainless steel exhibited over a thirty-fold decrease in Cr volatility compared with their uncoated counterparts. Effectively complete blocking of Cr volatility is expected, as uncoated portions of these samples were exposed during this testing.
- Demonstrated over 1,000 hours of low (<10 mΩ•cm<sup>2</sup>) and stable area specific resistance (ASR) values with coated stainless steel samples. Negligible chemical or physical changes were observed in sample post-mortem analyses.
- Developed thermochemical modeling of multielemental high temperature oxicermet coatings.

### Introduction

The Arcomac Surface Engineering, LLC (ASE) SECA project has focused on the development of protective and functional coatings to enable the use of inexpensive metallic alloys as SOFC ICs. Currently, the IC components of planar SOFC systems account for a dominant portion of the overall SOFC stack cost. Inexpensive ferritic stainless steels are under consideration for these components. However, when exposed to the typical SOFC operation environment, metallic alloys form blanketing oxide scales, which dramatically degrade SOFC performance and limit device lifetime. To date, deleterious issues with Cr volatility, electrical resistance, and thermal-mechanical and chemical incompatibilities have restricted the use of metallic alloys as ICs in planar SOFC systems. ASE has developed advanced coating deposition technologies, which show promise for resolving these issues in an economically-viable manner.

### Approach

To achieve the SECA cost and performance goals, the use of inexpensive ferritic stainless steels as IC components is under investigation. ASE is developing advanced, hybrid vapor plasma deposition technologies to establish protective coatings on commercially available alloys of interest as SOFC ICs. These coatings are aimed at inhibiting thermally grown oxide scale formation and outward Cr diffusion while retaining low area electrical resistivity at 750°C

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in air during long-term exposures. Desired coating compositions and architectures are determined through thermodynamic and transport modeling in addition to prior art. Appropriate deposition materials are acquired and deposition processes are designed and executed using ASE equipment. Coated samples are evaluated under exposures simulating SOFC IC operation, and sample coupon performance is analyzed. Results are employed to assist in developing new coating deposition process formulations. Promising coating systems from preliminary testing are then subjected to more prototypical SOFC IC conditions for further assessments. Concurrently, economic evaluations of coating process and interconnect component fabrication are ongoing.

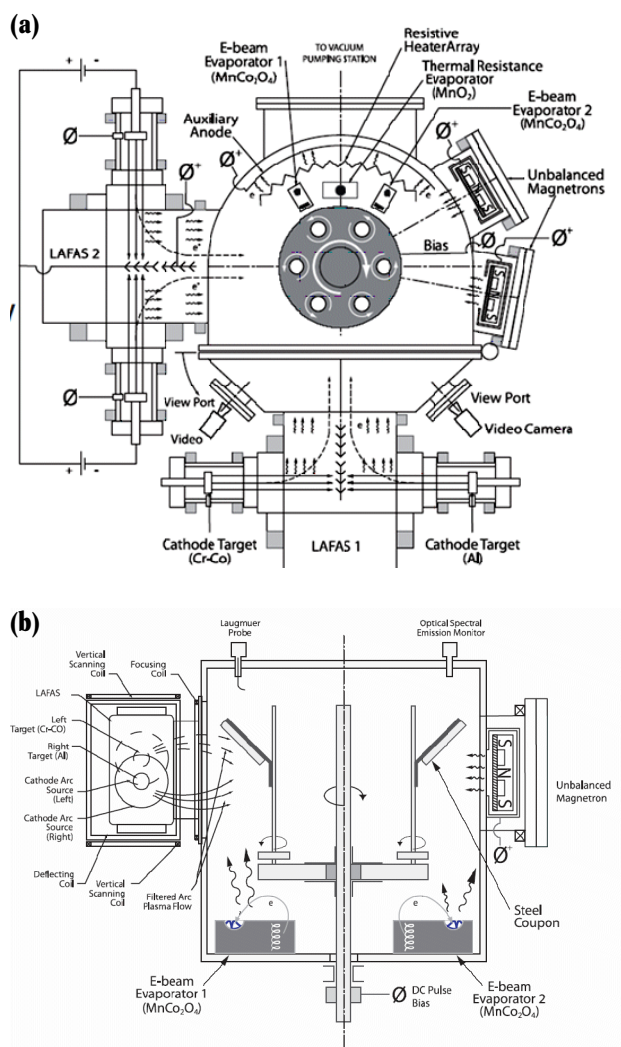
## Results

The patented filtered arc plasma source ion deposition (FAPSID) system developed by ASE utilizes two dual filtered cathodic arc LAFAD sources in conjunction with two UBM sputtering sources, two EBPVD evaporators and a thermal resistance evaporation source in one, universal vacuum chamber layout as illustrated in Figure 1 [1,2]. This system has demonstrated the capability to deposit nanocomposite, nanolayered coatings with a wide variety of compositions and architectures.

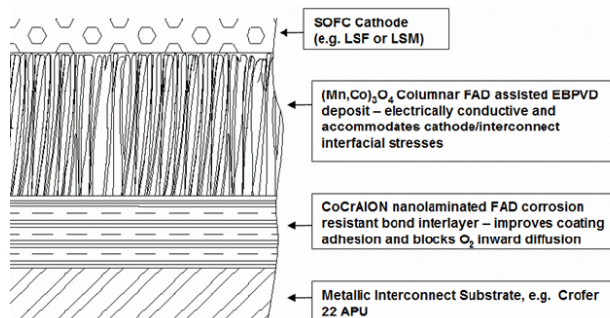
The present ASE two-segment hybrid coating approach is shown schematically in Figure 2. Filtered arc deposited, nanostructured coatings from the MCrAlYO system (where M = Co, Ti, Mn or Ni), are being investigated to comprise a lower, oxidation-resistant, adhesion-promoting bond coating segment. This layer is designed to function as an effective barrier, blocking both inward and outward diffusion of oxidizing species, while acting as an adhesion system to the upper coating segment. The transition metal dopants are selected to increase high temperature electronic conductivity by forming nanolaminated and/or nanocomposite thermistor-like oxicermet. Thermochemical modeling, using newly developed “TERRA” thermodynamic equilibrium calculation code is developed to estimate phase composition of multielemental oxicermet coatings and its interaction with SOFC IC operating environments. A matrix of these lower segment coatings have been successfully deposited with excellent adhesion to metallic substrates under consideration for SOFC interconnects. A  $(\text{Mn},\text{Co})_3\text{O}_4$  spinel coating deposited by the hybrid FAD-EBPVD process comprises an electrically conductive, Cr-retentive and SOFC cathode-compatible upper coating segment. Other hybrid deposition methods, employing filtered arc assisted thermal resistance evaporation are also being explored to deposit the upper segment coating. A matrix of upper segment coatings has been successfully deposited in combination with

and apart from the matrix of lower segment coating compositions.

SOFC IC-related behavior of coated and uncoated samples, i.e. high temperature oxidation, ASR, and

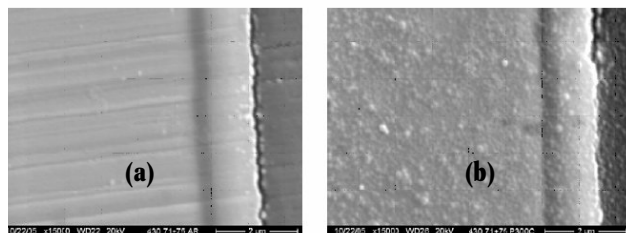


**FIGURE 1.** Schematic Illustration of the FAPSID Surface Engineering System, Showing (a) Top View and (b) Side View

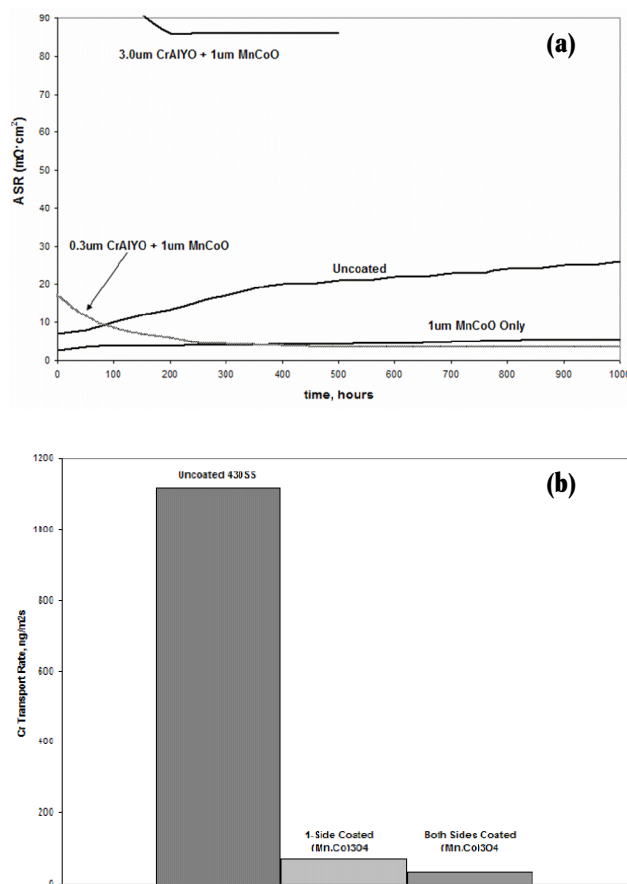


**FIGURE 2.** ASE's Two-Segment, Hybrid Coating Concept

Cr volatility have been investigated in collaboration with researchers at Montana State University, Pacific Northwest National Laboratory, Lawrence Berkeley National Laboratory and NASA-Glenn Research Center. Cross-section scanning electron microscopy (SEM) images in Figure 3 illustrate the thermal stability of the coating system. Figures 3a and 3b are of a two-segment



**FIGURE 3.** Cross Sectional SEM Images of Two-Segment Coating: FAD CrCoAlYO Nanostructured Bottom Segment Coating with Filtered Arc-Assisted EBPVD (Co,Mn)<sub>3</sub>O<sub>4</sub> Upper Segment Coating on 430 Stainless Steel: (a) As-Deposited and (b) Subsequent to 300 Hours Exposure to 800°C Air



**FIGURE 4.** (a) Summary of ASR Results on Coated and Uncoated Crofer 22 APU; (b) Cr Volatility Results from Coated and Uncoated 430 Stainless Steel

coating on 430 stainless steel before and after 300 hours exposure to 800°C air (throughout several thermal cycles), respectively. Figure 4 displays a summary of the ASR and Cr volatility results. Low ASR values, excellent adhesion, oxidation stability and promising Cr volatility data suggest the efficacy of the ASE two-segment coating approach.

## Conclusions and Future Directions

ASE has developed advanced coating deposition processes, which may enable the use of inexpensive metallic alloys as interconnect components in planar SOFC systems. Multilayered nanostructured oxicermet coatings, deposited by hybrid filtered arc assisted techniques are being investigated to meet SECA SOFC IC performance and cost requirements. A large-scale FAPSID surface engineering process, offering favorable economics through high yield and advanced hybrid design, is under investigation for deposition of protective coatings on SOFC ICs. Future work is dedicated to optimizing the composition and architecture of nanocomposite oxicermet coatings on prototype-size SOFC ICs made of ferritic stainless steels to further improve its thermal-chemical and mechanical stability, barrier properties and reduced ASR during long-term SOFC IC operation.

## FY 2006 Publications/Presentations

1. V.I. Gorokhovsky, "Filtered arc plasma assisted PVD coatings for SOFC metallic interconnects", Presented at the SECA Core Technology Review Meeting, Lakewood, CO, October 2005.
2. V.I. Gorokhovsky, P.E. Gannon, M.C. Deibert, R.J. Smith, A. Kayani, M. Kopczyk, D. VanVorous, Z. Gary Yang, J.W. Stevenson, S. Visco, C. Jacobson, H. Kurokawa, S.W. Sofie, "High temperature oxidation, Cr volatility and surface electrical conductivity of ferritic steel with filtered arc and hybrid filtered arc-assisted EBPVD coatings", Accepted for publication in the *Journal of the Electrochemical Society*.
3. P.E. Gannon, V.I. Gorokhovsky, M.C. Deibert, R.J. Smith, A. Kayani, P.T. White; Z. Gary Yang, J.W. Stevenson, S. Visco, C. Jacobson, H. Kurokawa, S.W. Sofie, "Enabling inexpensive metallic alloys as SOFC interconnects: an investigation into hybrid coating technologies to deposit nanocomposite functional coatings on ferritic stainless steels", Presented at the 135<sup>th</sup> annual TMS meeting and submitted for publication in the *International Journal of Hydrogen Energy*.
4. C. Collins, J. Lucas, T.L. Buchanan, M. Kopczyk, A. Kayani, P.E. Gannon, M.C. Deibert, R.J. Smith, D.S. Choi, V.I. Gorokhovsky, "Chromium volatility of coated and uncoated steel interconnects for SOFCs", Submitted to the 2006 International Conference on Metallurgical Coatings and Thin Films to be published in *Surface and Coatings Technology*.

5. A. Kayani, T.L. Buchanan, M. Kopczyk, C. Collins, J. Lucas, K. Lund, R. Hutchinson, P.E. Gannon, M.C. Deibert, R.J. Smith, D.S. Choi, V.I. Gorokhovsky, "Oxidation resistance at 800°C for magnetron-sputtered CrAlN coatings on 430 steel", Submitted to the 2006 International Conference on Metallurgical Coatings and Thin Films to be published in *Surface and Coatings Technology*.
6. V.I. Gorokhovsky, P.E. Gannon, M.C. Deibert, R.J. Smith, A. Kayani, S. Sofie, Z. Gary Yang, J.W. Stevenson, "Investigating hybrid filtered arc plasma source ion deposition technologies to deposit nanostructured functional coatings on ferritic stainless steels. *Part I: Deposition process parameters and basic coating characteristics*", Presented at the 2006 International Conference on Metallurgical Coatings and Thin Films.
7. P.E. Gannon, V.I. Gorokhovsky, M.C. Deibert, R.J. Smith, A. Kayani, S. Sofie, Z. Gary Yang, J.W. Stevenson, S. Visco, C. Jacobson, H. Kurokawa, "Investigating hybrid filtered arc plasma source ion deposition technologies to deposit nanostructured functional coatings on ferritic stainless steels. *Part II: Simulated solid oxide fuel cell interconnect performance*", Presented at the 2006 International Conference on Metallurgical Coatings and Thin Films.

## References

1. V. Gorokhovsky, US Patent No. 6,663,7552.
2. V.I. Gorokhovsky, "Filtered arc plasma assisted PVD coatings for SOFC metallic interconnects", Presented at the SECA Core Technology Review Meeting, Lakewood, CO, October 2005.